Thermodynamic Study on the Adsorption of Dioctadecyl Ether at Hexane/Water Interface

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The adsorption of dioctadecyl ether was studied at hexane/water interface, as functions of temperature, pressure, and mole fraction of dioctadecyl ether in hexane. The phase transition between expanded and condensed films was observed with decreasing temperature and increasing pressure and concentration. The thermodynamic quantities associated with the adsorption such as entropy, volume, and energy change were evaluated and comparison was made with the adsorbed films of 1-octadecanol at the same interface in which phase transition takes place. It is found that the dioctadecyl ether shows small negative discontinuous changes of the thermodynamic quantities with the transition from the expanded to the condensed films.

It is of great importance from the viewpoint of surface chemistry to clarify the structure and properties of adsorbed films at interface. In recent papers, we have shown that it can be achieved by applying the thermodynamic treatment developed previously.[1,2] Further we have revealed that the adsorbed film of 1-octadecanol at hexane/water interface shows a phase transition from an expanded to a condensed one and this phase transition is characterized by large negative discontinuous changes of the thermodynamic quantities associated with the adsorption.[3]

As an extension of this study, measurements are made for the adsorbed film of dioctadecyl ether at the same interface, in which the phase trandition takes place.

Experimental

Dioctadecyl ether was purified by repeated recrystallization. The purity was checked by the gas-liquid chromatography. Only one peak was obtained. Hexane used in this study was dehydrated and the impurity was removed by passing through an activated alumina column. Water distilled thrice from alkaline permanganate solution was used. The purity of hexane and water was always checked by the value of the interfacial tension between them.

The interfacial tension was measured by the pendant drop method. Detailed description of the apparatus and the method was given previously.[2,4]

Results

According to the phase rule the state of the system under consideration is completely specified by three independent variables and the structure and properties of interface are speculated by the thermodynamic quantities.[1,2] Then, the interfacial tension γ is measured as functions of temperature T and pressure p at the constant mole fraction of dioctadecyl ether in hexane x_1^0. Plots of γ against T under atmospheric pressure are shown in Fig. 1. At low concentrations the interfacial tension decreases linearly with increasing temperature. At higher concentrations, on the other hand, it increases. At intermadiate concentrations, the γ *vs.* T curve appeares to have a break point. This behavior is

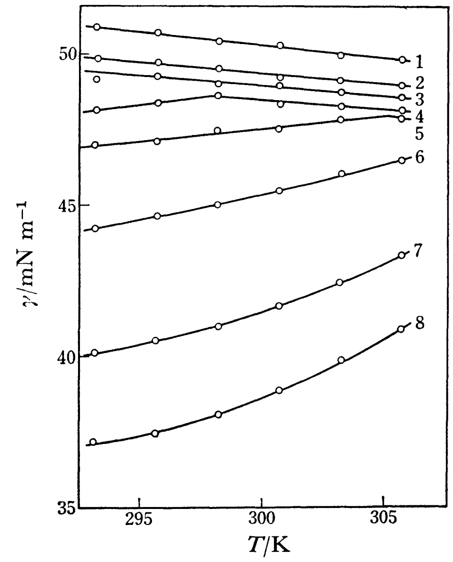

Fig. 1. Interfacial tension *vs.* temperature curves at various concentrations under 0.1 MPa.
1) $x_1^0=0$; 2) 7.88×10^{-5}; 3) 2.66×10^{-4}; 4) 3.11×10^{-4}; 5) 3.35×10^{-4}; 6) 4.00×10^{-4}; 7) 5.46×10^{-4}; 8) 7.19×10^{-4}.

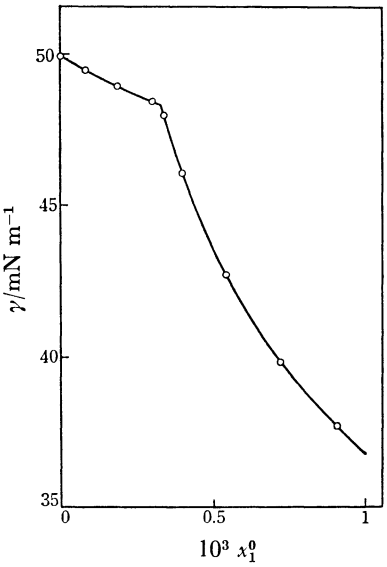

Fig. 2. Interfacial tension *vs.* mole fraction of dioctadecyl ether in hexane curve at 303.15 K under 0.1 MPa.

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similar to that of the adsorption of 1-octadecanol at hexane/water interface.[3] However, the break point is limited within a very narrow concentration range, *i.e.* between 2.7×10^{-4} and 3.6×10^{-4} of x_1^0 in this work. In Fig. 2 the interfacial tension *vs.* composition curve at 303.15 K is drawn which is prepared from Fig. 1. It has a sharp break point. In the study of the adsorption of 1-octadecanol, we observed that the first order phase transition is reflected on the γ *vs.* x_1^0 curves as a break point.[3] It is, therefore, conceivable that in the adsorbed film of dioctadecyl ether a similar phase transition takes place. Further, it is observed that at concentrations corresponding to the expanded state γ reaches rapidly its equilibrium value and at concentrations corresponding to the condensed state γ decreases gradually to an equilibrium value.

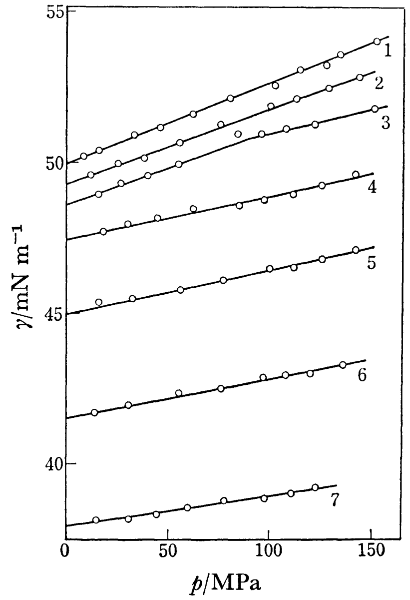

Fig. 3. Interfacial tension *vs.* pressure curves at various concentrations at 303.15 K.
1) $x_1^0=0$; 2) 1.02×10^{-4}; 3) 1.77×10^{-4}; 4) 3.54×10^{-4}; 5) 4.25×10^{-4}; 6) 6.04×10^{-4}; 7) 8.66×10^{-4}.

In Fig. 3 the interfacial tension is plotted against the pressure at various concentrations. The slope of γ *vs.* p curve is linear and positive except the curve at $x_1^0=1.77\times10^{-4}$ which has the break point at about 90 MPa. This figure is considerably different from that of 1-octadecanol.

Discussion

Taking into account that the mutual solubility of hexane and water is in fact negligible and dioctadecyl ether is soluble only in hexane, the thermodynamic quantities associated with the adsorption are estimated by applying the treatment developed previously.[1] The measurements being made on the solution of solute mole fraction below 1.0×10^{-3}, the solution is assumed to be ideal. Thus the interfacial density of surface active solute Γ_1^{H} is calculated by

$$\Gamma_1^{\mathrm{H}} = -(x_1^0/RT)(\partial\gamma/\partial x_1^0)_{T,p} \tag{1}$$

and other thermodynamic quantities are given as the derivatives of γ with T and p, that is

$$\Delta s = -(\partial\gamma/\partial T)_{p,x_1^0} \tag{2}$$

$$\Delta v = (\partial\gamma/\partial p)_{T,x_1^0} \tag{3}$$

and

$$\Delta u = \gamma - T(\partial\gamma/\partial T)_{p,x_1^0} - p(\partial\gamma/\partial p)_{T,x_1^0}, \tag{4}$$

where Δs, Δv, and Δu are the entropy, volume, and energy changes associated with the adsorption, respectively.

First Γ_1^{H} was calculated by Eq. 1 at various temperatures and pressures. Its value increases with concentration and pressure and decreases with temperature. An abrupt change is seen on the Γ_1^{H} *vs.* x_1^0 curve at the break point at which the expanded and condensed films coexist in equilibrium. Its values of the expanded and condensed states are 0.410 and 4.43 μmol m^{-2}, respectively. This significant behavior of dioctadecyl ether in the interface is revealed more clearly by drawing the interfacial pressure π *vs.* area per molecule A curve on the assumption that the adsorbed film is monomolecular. The π *vs.* A curve at 303.15 K and at 80 MPa is shown in Fig. 4 in which the curve of 1-octadecanol is also drawn. Although they seem somewhat different in shape, they are essentially identical with each other. In the condensed state the value of A of dioctadecyl ether is almost twice that of 1-octadecanol. Then it can be expected that the molecule adsorbes at the interface in such a way that its polar part is directed to the water phase and its two hydrocarbon chains are perpendicular to the interface. This restricted conformation might be related to the fact that the time dependence of interfacial tension is pronounced for the concentrated solutions.

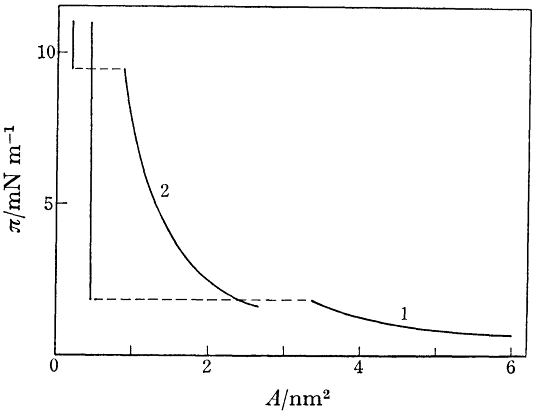

Fig. 4. Interfacial pressure *vs.* area curves at 303.15 K under 80 MPa. 1) Dioctadecyl ether; 2) 1-octadecanol.

It is now interesting to compare the entropy change of the adsorption on dioctadecyl ether and that of 1-octadecanol. The value of Δs evaluated by Eq. 2 is shown grafically as a function of x_1^0 at 303.15 K under atmospheric pressure in Fig. 5. The corresponding one of 1-octadecanol is also shown in this figure. It is seen apparently that dioctadecyl ether has a larger value than 1-octadecanol in the expanded state although

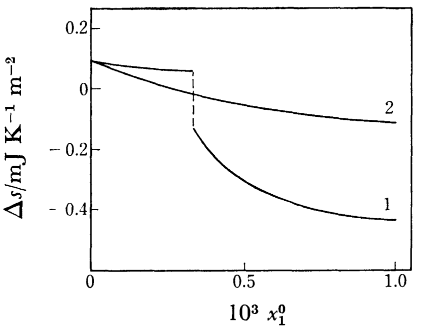

Fig. 5. Entropy change *vs.* concentration curves at 303.15 K under 0.1 MPa. 1) Dioctadecyl ether; 2) 1-octadecanol.

dioctadecyl ether has a more restricted conformation. We notice here that in such a comparison the difference between their interfacial densities is ignored. In Fig. 7A, Δs is plotted against Γ_1^H. As expected, the value of Δs of dioctadecyl ether is smaller than that of 1-octadecanol when compared at the same value of Γ_1^H. Thus we may say that the dioctadecyl ether molecule makes more negative contribution to Δs than 1-octadecanol molecule. It is also found that the entropy change associated with the phase transition, $\Delta s^c - \Delta s^e$, in which the superscripts *c* and *e* represent the condensed and expanded states, respectively, has a significantly small negative value compared with that of 1-octadecanol, *i.e.*, −1.4 mJ K^{-1} m^{-2} at 303.15 K and at 80 MPa. This small negative value might be ascribed in part to a loosely packed structure of the condensed film.

It is worthwhile to note that the fact that the break point on the γ *vs.* T curve is observed in a limited range of the concentration is related closely to a small difference between Δs^c and Δs^e. The variation of the equilibrium interfacial tension γ^{eq} between the expanded and condensed phases with temperature is given by[3]

$$(\partial\gamma^{eq}/\partial T)_p = -(\Delta s^c/\Gamma_1^{H,c} - \Delta s^e/\Gamma_1^{H,e})/(1/\Gamma_1^{H,c} - 1/\Gamma_1^{H,e}). \quad (6)$$

The left side of Eq. 6 is given by the slope of the locus of break points in Fig. 1; its value estimated roughly is *ca.* −0.12 mN m^{-1} K^{-1}. On the other hand, the numerical value of the right side, calculated from the experimental results of Figs. 3 and 5, is −0.087 mJ K^{-1} m^{-2} (mN m^{-1} K^{-1}). Taking account of some uncertainty in accuracy, the agreement of these numerical values is not unsatisfactory.

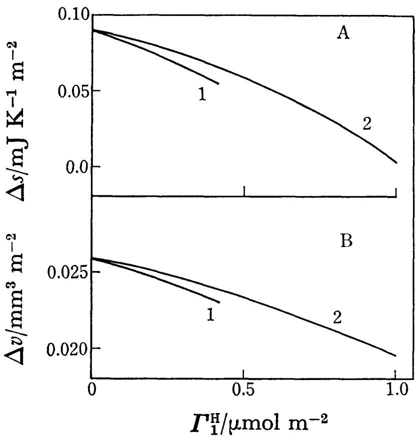

Fig. 7. A) Variation of entropy change with interfacial density at 303.15 K under 0.1 MPa.
B) Variation of volume change with interfacial density at 303.15 K under 0.1 MPa. 1) Dioctadecyl ether; 2) 1-octadecanol.

Lutton *et al.*[5] measured the interfacial tension as a function of temperature for the systems of monoglyceride and diglyceride solutions in cotton seed oil and water. Although the data are not complete, it is found that the difference in the slope of γ *vs.* T curve at the break point obtained for diglyceride is fairly smaller than that obtained for monoglyceride. Their data seem to support our observation that the phase transition of dioctadecyl ether is characterized by the small difference in Δs.

By use of Eq. 3 the value of Δv was evaluated from Fig. 3. The comparison of Δv *vs.* x_1^0 curves between dioctadecyl ether and 1-octadecanol is also made in Fig. 6. This figure is quite similar in appearance to Fig. 5. Further, a figure analogous to Fig. 7A is obtained when Δv is plotted against Γ_1^H (Fig. 7B). This fact indicates that the change in entropy associated with the adsorption is interrelated to the changes in volume. It is also explicable by the corresponding equation to Eq. 6 that the break point in the γ *vs.* p curve is observed only in a limited range of concentration as seen in Fig. 3.

Let us now calculate the energy of interface formation Δu by applying Eq. 4 to the above data. In Fig. 8, the

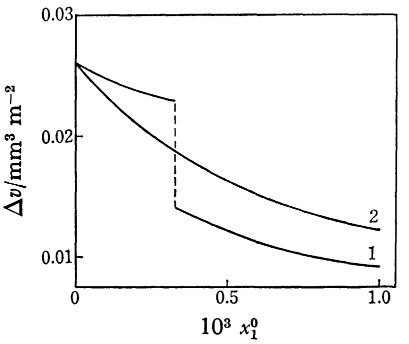

Fig. 6. Volume change *vs.* concentration curves at 303.15 K under 0.1 MPa. 1) Dioctadecyl ether; 2) 1-octadecanol.

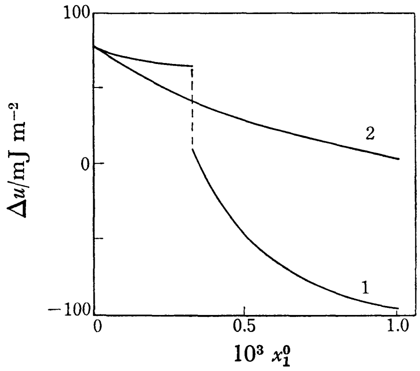

Fig. 8. Energy change *vs.* concentration curves at 303.15 K under 0.1 MPa. 1) Dioctadecyl ether; 2) 1-octadecanol.

value of Δu is plotted against x_1^0 at 303.15 K under atmospheric pressure. It varies with x_1^0 in a similar manner as Δs and Δv do. In the condensed state, however, its decrease with increase in x_1^0 is found to be relatively steep. This might reflect a gradual change of the structure of dioctadecyl ether film at the hexane/water interface with the concentration.

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